



Macromolecular cross-linked polybenzimidazole based on bromomethylated poly (aryl ether ketone) with enhanced stability for high temperature fuel cell applications

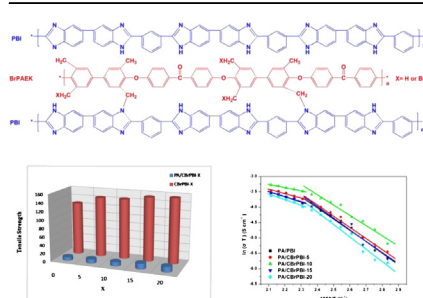
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HIGHLIGHTS

- A series of macromolecular cross-linked polybenzimidazole membranes were prepared.
- The macromolecule BrPAEK was first used as a cross-linker in PBI-based system.
- The CBrPBI-X membranes were prepared by an easy facile heating method.
- The chemical stability, oxidative stability and mechanical properties were improved.
- The results indicated that CBrPBI-20 was a promising candidate as HT-PEM.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 February 2013

Received in revised form

30 May 2013

Accepted 31 May 2013

Available online 11 June 2013

Keyword:

Macromolecular cross-linked

Polybenzimidazole

Bromomethylated poly (aryl ether ketone)

High temperature proton exchange

membrane

ABSTRACT

A series of macromolecular cross-linked polybenzimidazole (PBI) membranes have been successfully prepared for the high temperature proton exchange membrane fuel cell (HT-PEMFC) applications. Bromomethylated poly (aryl ether ketone) (BrPAEK) is synthesized and used as a macromolecular cross-linker, the cross-linking reaction can be accomplished at 160 °C using an easy facial heating treatment. The resulting cross-linked membranes CBrPBI-X (X is the weight fraction of the cross-linker) display excellent mechanical strength. After phosphoric acid (PA) doping, the mechanical strength and proton conductivity of the PA/CBrPBI-X membranes are both enhanced comparing with the pristine PA/PBI. Considering the tradeoff of the mechanical strength and proton conductivity, 10 wt% BrPAEK is demonstrated to be an optimum content in the matrix. For instance, the proton conductivity of PA/CBrPBI-10 is 0.038 S cm⁻¹ at 200 °C, which is higher than that of pristine PA/PBI with the proton conductivity of 0.029 S cm⁻¹ at the same temperature. Other properties of the cross-linked membranes are also investigated in detail, including the oxidative stability, solubility and thermal stability. All the results indicate that the PA/CBrPBI-10 membrane has the potential application in HT-PEMFCs.

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1. Introduction

Polybenzimidazole (PBI) is a kind of heterocyclic high-performance polymer with high glass transition temperature, high thermal stability, excellent chemical resistance and mechanical properties [1–3].

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Phosphoric acid-doped polybenzimidazoles (PA–PBIs) are supposed to be the most appealing polymers electrolyte membranes for high temperature proton exchange membrane fuel cells (HT-PEMFCs) [4–6]. Proton exchange membranes (PEMs) are the core material of PEMFCs and need to offer an attractive combination of chemical, physical, mechanical, and electrochemical properties [7–9]. As a commercially available PEM, Nafion has been widely studied due to its high proton conductivity, excellent chemical and mechanical

properties [10,11]. However, the high cost and overly dependent on humidity, poor methanol crossover, as well as other problems limit the large-scale commercialization of PEMFCs [12–15]. Thus, there are numerous efforts to develop alternatives to Nafion, PEMs based on PA–PBI are extensively studied for they can work above 130 °C which is preferable from the point of water and heat management [16–20]. However, the conductivity of PA–PBI is affected by the doping levels and relative humidity. Higher doping levels lead to higher proton conductivity but poorer mechanical properties, so there is a tradeoff between doping levels and mechanical properties [5,21].

To overcome the deficiencies, several methods have been explored. An efficient way is to prepare cross-linked membranes. Li *et al.* reported a kind of cross-linked polybenzimidazole membrane using *p*-xylene dibromide as a cross-linker [22]. Epoxy based cross-linked polybenzimidazole was prepared by Han *et al.*, which displayed enhanced mechanical and chemical stability [23]. The structures of cross-linkers greatly affect the properties of cross-linked membranes. For instance, in our previous work, we have prepared two kinds of epoxy-based cross-linked polybenzimidazoles, one cross-linker was 4,4'-diglycidyl(3,3',5,5'-tetramethylbiphenyl) epoxy resin (TMBP), the other was 1,3-bis(2,3-epoxypropoxy)-2,2-dimethylpropane (NGDE) [23,24]. The most obvious difference between these two cross-linkers was the chemical structure, the former was rigid aromatic ring structure and the latter was totally flexible alkyl chain structure. The results indicated that cross-linked PBI membranes using rigid structure cross-linker displayed better combination properties of mechanical strength, oxidative stabilities, high doping levels and proton conductivity. What's more, several researchers have prepared cross-linked polymer membranes using macromolecular cross-linkers, which resulted in high cross-linking density and excellent mechanical properties and chemical stabilities [25–27].

Herein, we prepared a series of novel cross-linked polybenzimidazole using a macromolecular cross-linker with rigid aromatic ring structure, which is bromomethylated poly (aryl ether ketone) (BrPAEK). For the BrPAEK, we can quantitatively control the contents of the bromine tethered to the benzyl groups. To our best knowledge, there is no report about the BrPAEK being used as the cross-linker in the PBI-based systems. The cross-linked membranes were prepared through a gentle and facile heating method. In order to optimize the resulting cross-linked membranes' performance, we blended various amounts of BrPAEK into PBI matrix. The mechanical properties, oxidative and chemical stability of the cross-linked membranes were significantly improved. All the cross-linked membranes were doped with the phosphoric acid (PA) and the proton conductivity of PA/CBrPBI-X (X is the weight fraction of the cross-linker) was elevated comparing with the pristine PA/PBI. Other properties were assessed as high-temperature PEMs in detail. All the results showed that BrPAEK was a suitable macromolecular cross-linker and the cross-linked membranes would be potentially used in HT-PEMFCs.

2. Experimental section

2.1. Materials

Monomers 3,3'-diaminobenzidine (DAB), diphenyl-*m*-phthalate (DPIP), 3,3',5,5'-tetramethyl-4,4'-biphenol (TMbP) and *N*-bromosuccinimide (NBS) were purchased from Shanghai Jiachen Chemical Co. 4,4'-Difluorobenzophenone (DFBP) was obtained from Yanbian Longjing Chemical Co., and benzoyl peroxide (BPO) used as initiator was provided from Lanzhou Aokai Chemical Co. and used without further purification. All the other reagents were obtained were of commercially available and treated by a standard method before use.

2.2. Synthesis of PAEK

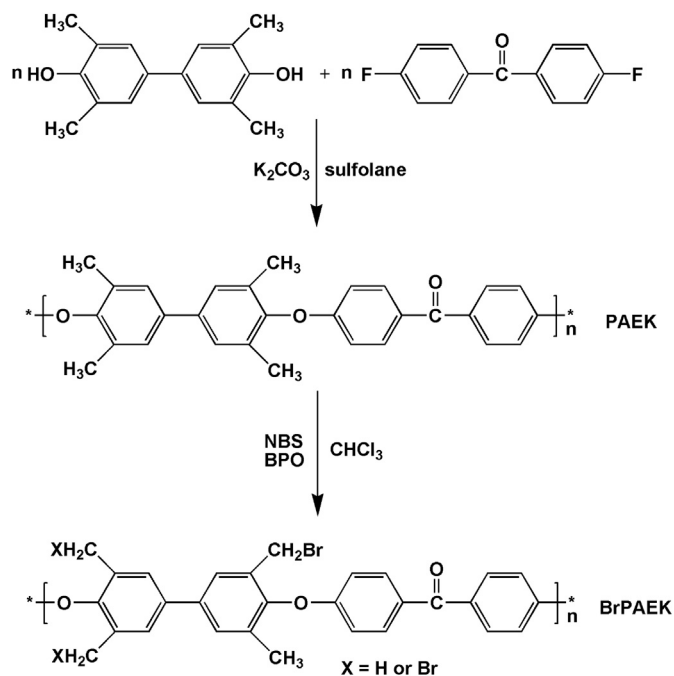
As shown in Scheme 1, poly (aryl ether ketone) (PAEK) was synthesized as follows: (i) DFBP (50 mmol), TMbP (50 mmol), anhydrous potassium carbonate (K_2CO_3) (55 mmol), sulfolane (51 mL) and toluene (30 mL) were added to a 500 mL three-necked flask equipped with a mechanical stirrer, a Dean–Stark trap, and a nitrogen inlet; (ii) The reaction mixture was heated and stirred slowly until the toluene began to reflux at about 140 °C, kept at this temperature for about 3 h and then removed the toluene; (iii) raising the reaction temperature to 210 °C and holding at this temperature until the viscosity of the mixture was high enough; (iv) pouring the viscous solution into cold water; (v) the obtained polymer was thoroughly washed with deionized water and dried in a vacuum oven at 120 °C for 24 h.

2.3. Synthesis of bromomethylated poly (aryl ether ketone) (BrPAEK)

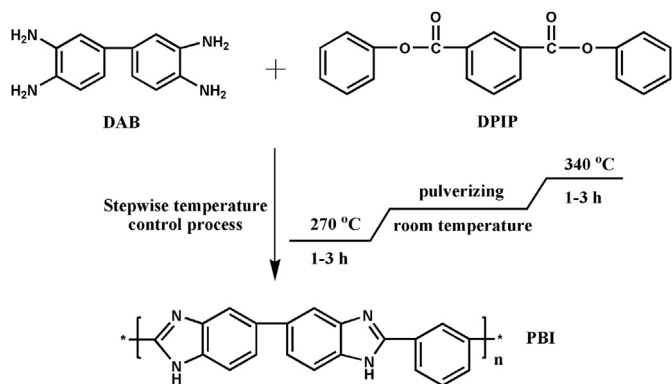
BrPAEK was synthesized by a one-step method, which was clarified in Scheme 1. The bromination process was carried out in chloroform, NBS acted as the bromination reagent and BPO initiated the radical reaction. The specific procedure was as follows: PAEK (5 mmol), NBS (45 mmol), BPO (0.05 g), and chloroform (50 mL) were added to a 250 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser. The mixture was slowly heated to 84 °C to reflux and the mixture turned to blood red. After the system was cooled, it was poured into a mixture of ethanol and water. A yellow precipitate was obtained and thoroughly washed with ethanol for several times. The resulting BrPAEK was dried in a vacuum oven at 60 °C for 24 h.

2.4. Synthesis of polybenzimidazole (PBI)

Scheme 2 shows the synthesis process of PBI. A typical two-step melting polymerization was performed as follows: (i) DAB (25 mmol) and DPIP (25 mmol) were added to a 500 mL three-necked flask equipped with a mechanical stirrer and a nitrogen



Scheme 1. The synthesis process of PAEK and BrPAEK.



Scheme 2. The synthesis process of PBI.

inlet/outlet. Then the system was heated in an oil bath to change the mixture from solid to liquid and stirred quickly and continuously. The viscosity of the mixture became larger with the increasing temperature and held at 270 °C for 1–3 h. Then the prepolymer was obtained and pulverized carefully into powder. (ii) The powder was added to a three-necked flask and heated at 340 °C for 1–3 h. Finally, PBI was obtained.

2.5. Fabrication of cross-linked membranes (CBrPBI)

CBrPBI-X (X is the weight fraction of BrPAEK) membranes were obtained by progressive heating treatment (Scheme 3). The detailed fabrication procedure was as follows: certain content of PBI and cross-linker BrPAEK was dissolved in N,N-dimethylacetamide (DMAc) to achieve a 10 wt.% solution and the weight fraction of the cross-linker in the matrix was 5%, 10%, 15% and 20%, respectively. The mixture was stirred for 4 h and then casted on clean glass plates. To evaporate the solvent, the casted mixture was dried in the oven at 60 °C for 24 h. The cross-linking treatment was performed at 160 °C for 3 h in a vacuum oven and the resulting cross-linked membranes were denoted as CBrPBI-5, CBrPBI-10, CBrPBI-15 and CBrPBI-20, respectively. The thickness of CBrPBI-X membranes was in the range of 45–55 μm.

2.6. Doping procedure

The PA doped membranes were obtained by soaking the cross-linked membranes in a 14.6 mol L⁻¹ of PA solution at 120 °C for 24 h to be fully saturated. Then, the samples were taken out and wiped immediately with tissue paper and dried in a vacuum oven at 120 °C to remove absorbed water thoroughly and weighed

immediately to calculate the PA doping level which was calculated as the molar number of PA per repeat unit of PBI.

The PA level was determined by comparing the weight changes between undoped (W_{dry}) and vacuum dried doped membranes (W_{acid}). The corresponding equation was listed as follows:

$$\text{PA level} = \frac{(W_{acid} - W_{dry}) / M_{PA}}{(W_{dry}(1 - X\%)) / M_{PBI}} \quad (1)$$

where M_{PA} and M_{PBI} represent the molecular weights of phosphoric acid and repeat unit of PBI, respectively. X is the weight percent of the cross-linker in the membrane.

2.7. Characterization and measurements

2.7.1. Structural characterization

The ¹H NMR spectra were performed on a 500 MHz Bruker Avance 510 spectrometer at 298 K with deuteriochloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the standard. The bromine content per repeat unit of the BrPAEK was measured by integration and comparison of the ¹H NMR signals arising from protons of the methyl and the brominated methyl. The degree of bromine groups (D_{Br}) was calculated by the following equation:

$$D_{Br} = \frac{12A_{H2}}{3A_{H2} + 2A_{H1}} \quad (2)$$

where A_{H2} is the peak area of brominated methyl protons, and A_{H1} is assigned to the peak area of methyl protons.

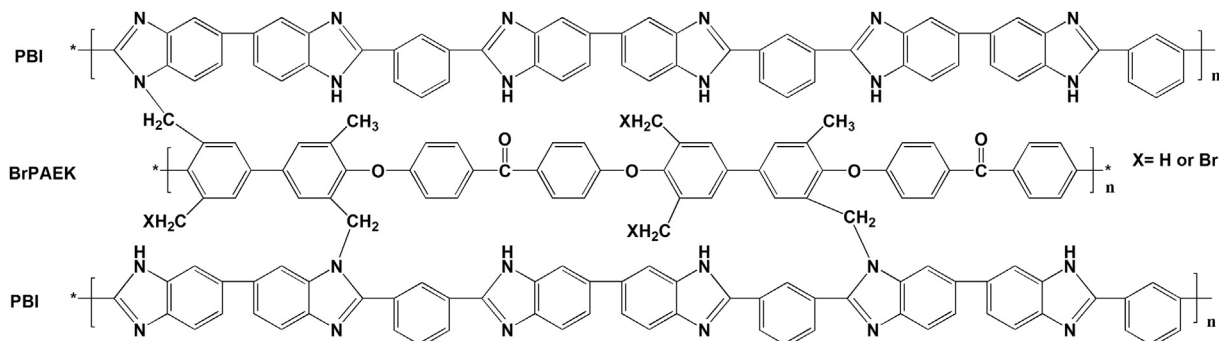
Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet Impact 410 spectrometer. The samples for spectra measurement were prepared by dispersing the powder samples in dry KBr disks and measured in the range of 4000–400 cm⁻¹.

2.7.2. Solubility test

Generally, solubility test in common solvents was used to characterize the cross-linking of the membranes. The small pieces of cross-linked CBrPBI-X membranes and pristine PBI membrane were immersed in DMAc for 24 h at 80 °C. Then the residual samples in the DMAc solution were collected, dried, and weighed. The weight residue of the cross-linked membranes was then obtained from the weight losses and calculated by the following formula:

$$\text{Weight residue}(\%) = \frac{W_b - W_a}{W_b} \times 100 \quad (3)$$

where W_b is the weight of dry membranes before being immersed in DMAc, W_a is the weight of cross-linked membranes after being immersed in DMAc.



Scheme 3. A schematic representation of the structure of macromolecular cross-linked CBrPBI-X membrane.

2.7.3. Oxidative stability

The oxidative stability was investigated by immersing small pieces of cross-linked membranes in Fenton's reagent (3% H₂O₂ solution containing 4 ppm Fe²⁺) at 70 °C. After each 24 h, the samples were collected by filtering and cleaned with deionized water several times, then dried at 120 °C for more than 20 h in a vacuum oven and recorded the remaining weight.

2.7.4. Thermal stability

The thermogravimetric analysis (TGA) measurements were performed on a Pyris 1TGA (Perkin Elmer) under nitrogen atmosphere. Before measurement, both undoped and doped samples were preserved in a vacuum oven at 120 °C to remove absorbed moisture and residual solvent. Then the samples were cooled to 80 °C and reheated to 800 °C at a heating rate of 10 °C min⁻¹.

2.7.5. Mechanical properties

The mechanical properties of the membranes were obtained by a SHIMADZU AG-I 1KN in ambient atmosphere at a test speed of 2 mm min⁻¹. The size of the samples is 4 mm × 15 mm. Each sample was tested at least 10 times to reach an average value.

2.7.6. Proton conductivity

The proton conductivities of the PA fully saturated membranes (1 cm × 4 cm) were measured by a four-electrode ac impedance method over a frequency range of 10–10⁷ Hz from 100 to 200 °C using a Princeton Applied Research Model 2273A Potentiostat/potentiostat/galvanostat/FRA. The measurement was carried out under anhydrous conditions. The proton conductivity was calculated by the following formula:

$$\sigma = \frac{L}{RA} \quad (4)$$

where σ is the proton conductivity in S cm⁻¹, L is the distance between the two electrodes, R is the resistance of the membrane, and A is the cross-sectional area of the membrane.

3. Results and discussion

3.1. Characterization of PBI and BrPAEK

As shown in Fig. 1, the representative ¹H NMR spectrum of PBI using deuterated dimethyl sulfoxide (DMSO-d₆) solutions, the peak

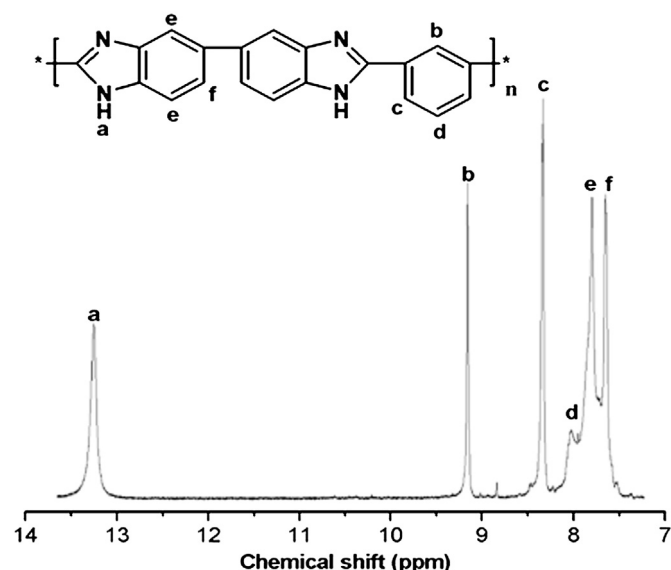


Fig. 1. ¹H NMR spectrum of PBI.

of 13.26 ppm was assigned to the amine protons on the benzimidazole moieties and peaks of 7.60–9.16 ppm represented the proton on the aromatic groups. BrPAEK was synthesized via a radical bromination reaction with a mild brominating agent (NBS) and an initiator (BPO). Fig. 2 shows the ¹H NMR spectra of PAEK and BrPAEK, the peaks at 2.22–2.23 ppm were assigned to the methyl groups of PAEK, while the new peaks at 4.41–4.44 ppm were attributed to the hydrogen atoms of the bromomethylene groups in BrPAEK. It was obviously that there was a differentiation of H₃, which was because of the different substituted groups in the benzyl site. Henceforth, the ¹H NMR spectra suggested that the BrPAEK was successfully synthesized, and the degree of bromination was 1.93 (by ¹H NMR).

The FT-IR spectra of PBI and CBrPBI-X membranes are shown in Fig. 3. The typical absorption peak at 623 cm⁻¹ was assigned to the stretching vibration of C–Br and then it disappeared completely in the CBrPBI-X membranes, which indicated that the bromomethylene groups of BrPAEK successfully reacted with the imidazole rings of PBI. The vibration at 1646 cm⁻¹ was attributed to the C=O stretching vibrations of BrPAEK and the peaks at 804 cm⁻¹, 1410 cm⁻¹ and 1620 cm⁻¹ were assigned to the typical absorption of imidazole ring of PBI.

3.2. Solubility of cross-linked membranes

From a general point of view, the solubility of the membranes was implemented to testify the formation of cross-linked networks in the membranes. All the membrane samples were immersed in a certain amount of N,N-dimethylacetamide (DMAc) solution at 80 °C for 24 h and then the weight residue was calculated. It can be clearly seen in Fig. 4, the pristine PBI membranes can be completely dissolved in common organic polar solvents, such as DMAc, however, the cross-linked membranes did not dissolve in those solvents but significantly swollen. The residue weight of the cross-linked membranes was in the range of 46.40–71.35% as shown in Fig. 5, which indicated that the cross-linked networks were successfully formed in the system. Moreover, the residue weight increased with higher amounts of BrPAEK, which also indicated that the cross-linking density increased with the increasing amount of macromolecular cross-linker.

3.3. Oxidative stability

It is of great importance for the PEMs with long-term performance [28,29]. Usually, the chemical stability of the membranes

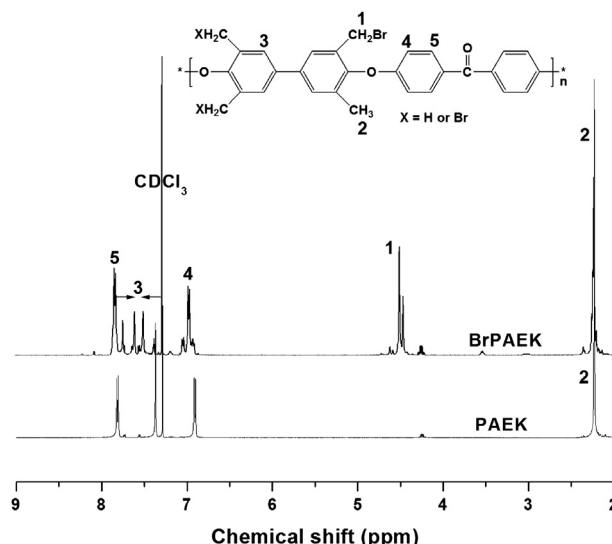


Fig. 2. ¹H NMR spectra of PAEK and BrPAEK.

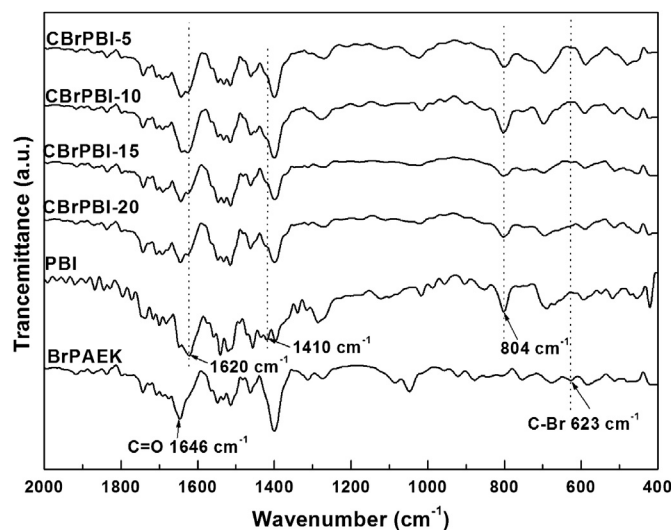


Fig. 3. FTIR spectra of BrPAEK, PBI and macromolecular cross-linked CBrPBI-X.

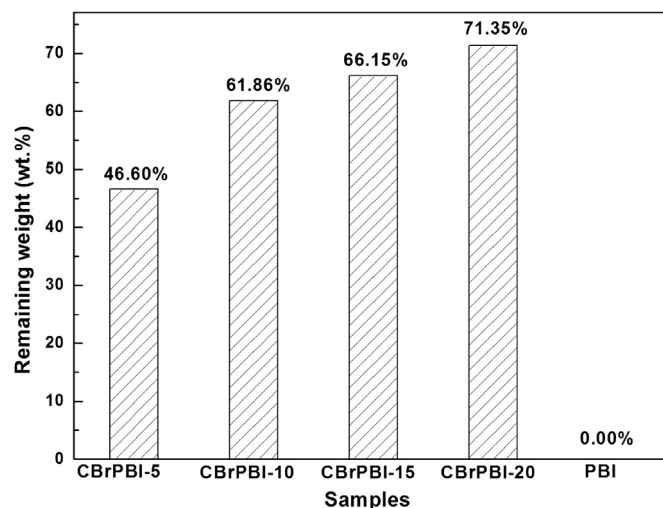


Fig. 5. Weight residue of PBI and CBrPBI-X membranes after the solubility test in DMAc at 80 °C for 24 h.

was testified by Fenton's reagent to indicate the long-term durability of PEMs. In the present work, the oxidative stability was investigated by immersing all the membranes in Fenton's reagent at 70 °C. The samples were taken out, washed and dried every 24 h and the degradation of all the samples was calculated by the weight loss. As shown in Fig. 6, the cross-linked membranes displayed improved oxidative stability over the pristine PBI membrane. After the first 24 h, the remaining weight of pristine PBI decreased to 76.9%, while that of the cross-linked membranes was in the range of 93.4–94.5%. All the cross-linked membranes displayed a similar trend and the results indicated that cross-linking could improve the oxidative significantly [22,23,30].

3.4. Thermal stability

The thermal properties of PBI, CBrPBI-X, BrPAEK, PA/PBI and PA/CBrPBI-X membranes were investigated by thermogravimetric analysis (TGA). As shown in Fig. 7 (a), pristine PBI membrane

displayed excellent thermal stability, which had only a one-step degradation pattern at around 600 °C. This weight loss was attributed to the decomposition of the main polymer chain. The BrPAEK membrane showed the first weight loss at about 265 °C, which was corresponded to the C–Br bond cleavage, while the second decomposition temperature above 500 °C was associated with the main polymer chain degradation. For the cross-linked CBrPBI-X membranes, they displayed a similar tendency. Compared with other cross-linked membranes, CBrPBI-5 showed higher decomposition temperature, whose $T_{d(5\%)}$ and $T_{d(10\%)}$ were 328 °C and 417 °C, respectively. After PA doping procedure, the thermal properties of all the membranes declined sharply and all the curves displayed similar trend. Compared with the pristine PA/PBI, the PA/CBrPBI-X membranes showed poor thermal stability. For instance, the $T_{d5\%}$ of PA/PBI was 309.2 °C and that of PA/CBrPBI-X was in the range of 215.1–225.54 °C. It can be also seen from Fig. 7(b) that the first degradation step begins at about 160 °C, which was attributed to the condensation reaction of phosphoric acid to form pyrophosphoric acid. The results are similar to the previous literatures [23,24,31]. The second step was observed at about 600 °C, which was assigned to the degradation of the PBI

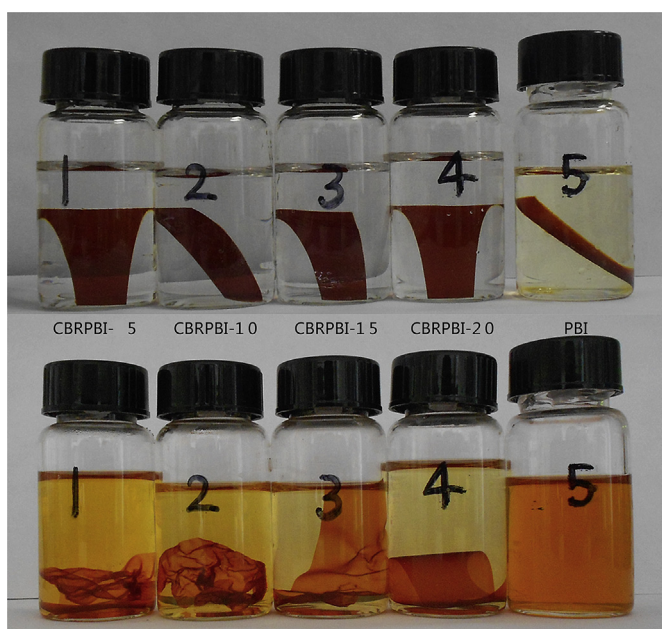


Fig. 4. Photographs of the membranes before and after dissolving in DMAc at 80 °C.

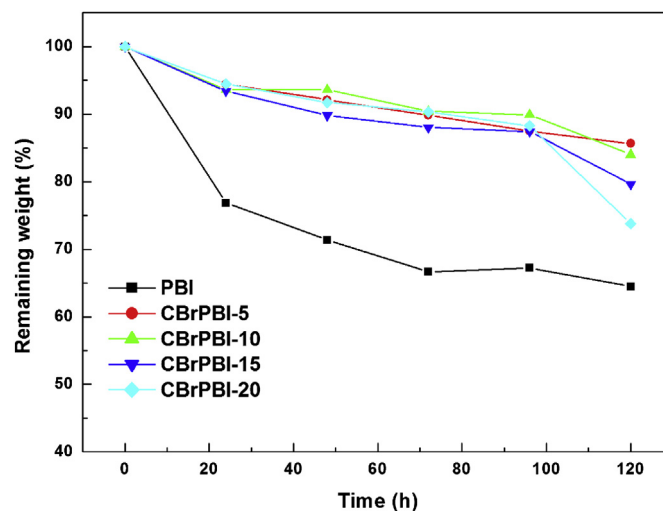


Fig. 6. Membrane degradation in 3% H₂O₂ containing 4 ppm Fe²⁺ at 70 °C.

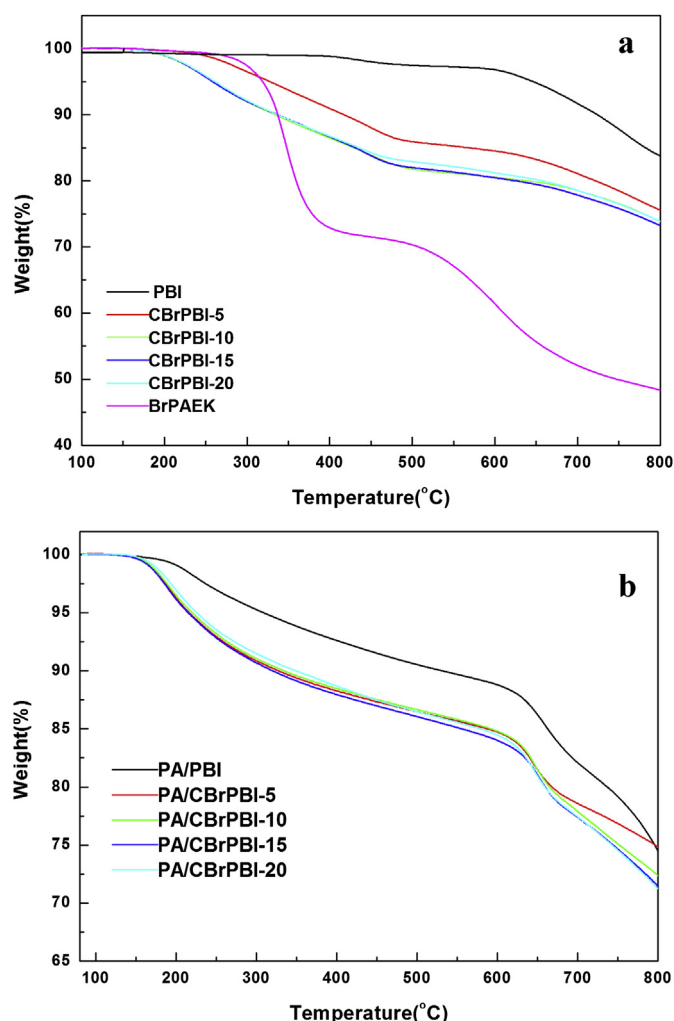


Fig. 7. TGA curves of undoped (a) and PA doped (b) PBI, CBrPBI-X.

main chain and the further dehydration of pyrophosphonic acid to polyphosphoric acid. From these results, it can be concluded that these PA/CBrPBI-X membranes are still thermal stable below 200 °C, which is within the temperature range of fuel cell applications.

3.5. Mechanical properties

The mechanical properties of proton exchange membranes are extremely important from the viewpoint of applications. Cross-linking is an effective way to improve the mechanical strength which can be indicated from the results listed in Table 1. Fig 8 shows the actual tensile curves of undoped and doped membranes at

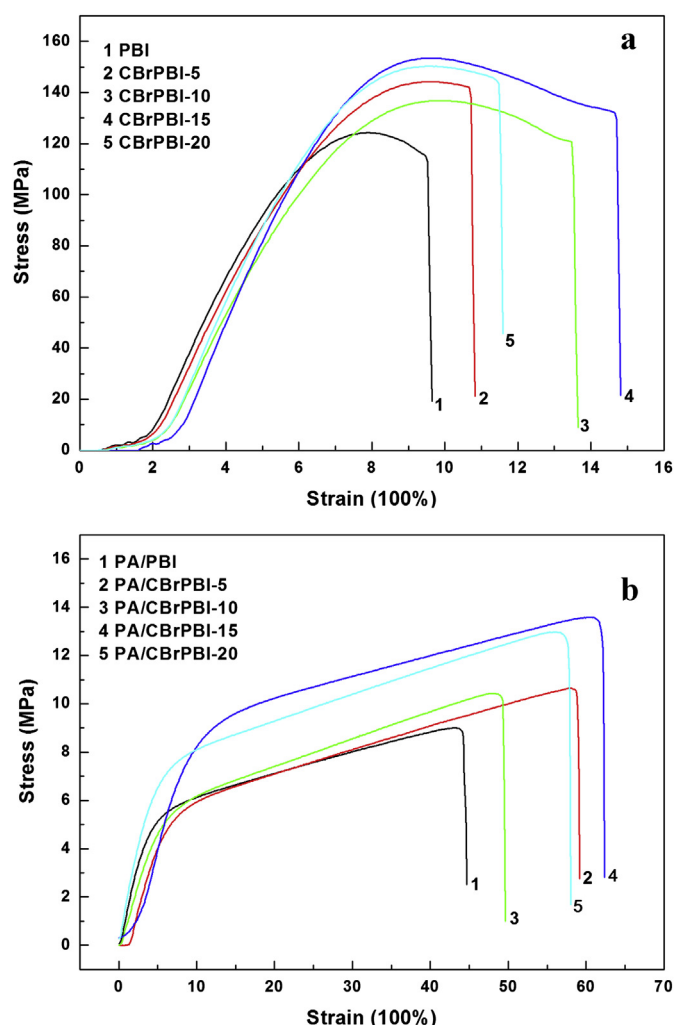


Fig. 8. Stress–strain curves of undoped (a) and PA doped (b) PBI, CBrPBI-X membranes.

room temperature. For the undoped membranes, the Young's modulus of the cross-linked membranes were slightly higher than the pristine PBI membrane, which were in the range of 2.1–2.3 GPa. Moreover, the tensile strength was much improved after cross-linking, that of CBrPBI-20 was as high as 155.2 MPa and other cross-linked membranes were in the range of 143–153 MPa. The elongation at break of the cross-linked membranes was between 9.9–14.6%. In comparison, the tensile strength of Zhang's cross-linked SPEEK-X membranes using a macromolecular cross-linker was in the range of 51.4–62.5 MPa [26], and other cross-linked PBIs, such as that of Xu's SOPBI-X was in the range of 81–98 MPa [32], and that of Li's cross-linked PBI-DCMP membranes was in the

Table 1

The mechanical properties of PBI and cross-linked CBrPBI-X membranes before and after doping in PA solutions and the PA doping levels.

Samples	Undoped			Doped (120 °C)			
	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	PA level
PBI	2.0 ± 0.1	126.4 ± 4.4	10.0 ± 2.1	110.1 ± 13.8	8.8 ± 0.5	44.8 ± 5.5	6.85
CBrPBI-5	2.2 ± 0.1	143.8 ± 4.8	9.9 ± 1.4	110.5 ± 15.2	10.3 ± 1.3	57.3 ± 9.0	7.16
CBrPBI-10	2.1 ± 0.1	144.3 ± 5.2	11.37 ± 2.0	111.7 ± 7.1	10.2 ± 0.3	49.3 ± 2.4	7.84
CBrPBI-15	2.3 ± 0	153.0 ± 5.7	12.5 ± 6.3	112.8 ± 1.3	13.5 ± 1.3	54.7 ± 10.2	7.02
CBrPBI-20	2.1 ± 0.1	155.2 ± 3.0	14.6 ± 7.6	155.6 ± 3.7	13.5 ± 1.2	60.7 ± 7.2	6.67

range of ~30–85 MPa [33]. The results indicated that these membranes were strong and tough enough with the introduction of macromolecular cross-linker. After doping at 120 °C for 24 h, the mechanical strength deteriorated seriously. For instance, the tensile strength of pristine PBI membrane decreased to 8.8 MPa, while that of the cross-linked membranes were decreased to 10.3–13.5 MPa. However, the values of elongation at break improved because of the plasticizing effect of phosphoric acid. Hence, introduction of macromolecular cross-linker efficiently improved the mechanical strength.

3.6. Proton conductivity

The proton conductivity is one of the most important factors to be considered as the performance of a fuel cell. In this work the proton conductivity of the membranes with different BrPAEK contents was measured under anhydrous conditions. The proton conductivity was affected by several factors, such as the polymer structure, proton mobility and water content. For the acid doped PBI-based membranes, the acid doping level, temperature and ambient humidity influenced the proton conductivity significantly [22]. Under anhydrous conditions, we should make sure remove the absorbed humidity, so the membranes were kept in the oven at 120 °C for several hours before the conductivity measurement. The proton conductivity values were obtained at a cooling process from 200 °C to 80 °C.

In order to understand the mechanism for the membrane proton conductivity, Arrhenius plots of the $\ln(\sigma)$ against the inverse of temperature is necessary to be analyzed. The proton conductivity usually follows a simple Arrhenius law in a proton-hopping dominant mechanism, which can be described by the equation:

$$\ln(\sigma) = \ln(\sigma_0) - \frac{E_a}{RT} \quad (5)$$

where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), E_a is an activation energy for conduction, and σ_0 is a pre-exponential factor. Fig. 9 presents the Arrhenius plots of the PA/PBI and PA/CBrPBI- X membranes and the E_a values of all the membranes. It can be clearly seen from Fig. 9(a), the proton conductivity of all the membranes increased with higher temperature. The CBrPBI-10 membrane showed the highest proton conductivity of 0.038 S cm^{-1} at 200 °C, while that of the CBrPBI-20 membrane was the lowest of 0.027 S cm^{-1} at 200 °C. Hence, the content of cross-linker had an optimum value of 10 wt%. Moreover, the temperature dependence of the proton conductivity for all the membranes displayed a straight line for the temperature range from 160 °C to 80 °C. However, the slopes of the curves decreased and deviated from the straight lines at temperature higher than 160 °C. So the mechanism of the proton conductivity was different between these two parts. At temperature below 160 °C, the proton conduction mechanism in the PA doped membranes was assumed to be attributed to conduction through a chain of acid molecules as well as the interaction of polymers and the phosphoric acid [34]. The imidazole rings were protonated by the phosphoric acid and thus the protons hopped between the PBI backbones and the acid facilitated by the hydrogen bond forming and breaking processes. As the temperature higher than 160 °C, a counter effect happened to form the oligomeric species such as the dimer (pyrophosphoric acid, $\text{H}_6\text{P}_2\text{O}_7$), trimer (meta- or tri-polyphosphoric acid, $\text{H}_8\text{P}_3\text{O}_{10}$), and larger fused structures formed at high temperature, which resulted in slower increase of the conductivity. So when the temperature was higher than 160 °C, the E_a values decreased dramatically due to lack of movable protons. However, high temperature could effectively enhance the Brownian motion and attributed to faster proton transferring, so the overall trend of the

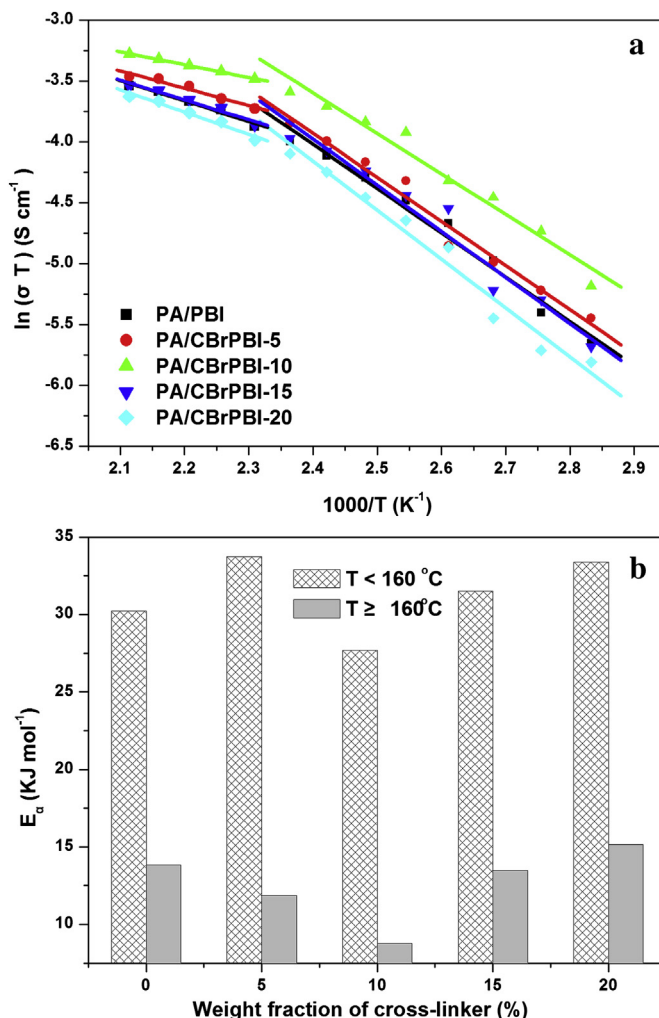


Fig. 9. Arrhenius plots of PA/PBI and PA/CBrPBI- X membranes (a) and the values of E_a of PA/PBI and PA/CBrPBI- X membranes (b).

conductivity was increasing with elevated temperature. The activation energy for proton conduction should be between 14 kJ mol^{-1} and 40 kJ mol^{-1} [35]. As shown in Fig. 9(b), the E_a value of PA/CBrPBI-10 was the lowest comparing with other membranes, no matter at temperature lower than 160 °C ($27.68 \text{ kJ mol}^{-1}$) or higher than 160 °C (8.77 kJ mol^{-1}), so it displayed the most improved proton conductivity due to the high PA doping level and low proton conducting activation energy. All the results above indicated that the macromolecular cross-linking method enable the PBI membranes to obtain both high PA doping levels and sufficient mechanical strength, as well as the relative high proton conductivity.

4. Conclusion

We demonstrated a novel method of obtaining a series of macromolecular cross-linked CBrPBI- X (X is the weight fraction of the cross-linker) membranes. The reaction between the imidazole rings of PBI and the bromine tethered to the benzyl groups of BrPAEK could be easily completed by a facile heating treatment. Compared with the pristine PBI membrane, the cross-linked membranes displayed improved mechanical strength, oxidative and chemical stability. For the PA doped membranes, the mechanical strength and proton conductivity of the PA/CBrPBI- X membranes were both enhanced comparing with the pristine PA/PBI. We obtained an optimum

content of macromolecular cross-linker (BrPAEK) of 10 wt% through a comprehensive evaluation of the tradeoff between proton conductivity and mechanical strength. In conclusion, introducing the macromolecule as a cross-linker in the PBI matrix was an effective way to improve the proton conductivity without sacrificing the mechanical strength, and PA/CBrPBI-10 in this work could be a promising candidate as HT-PEM.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (Grant No.21074044 and 21104022).

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List of symbols

PBI: polybenzimidazole
 PAEK: poly (aryl ether ketone)
 BrPAEK: bromomethylated poly (aryl ether ketone)
 CBrPBI-X: macromolecular cross-linked polybenzimidazole membranes
 PEMs: proton exchange membranes
 PEMFCs: proton exchange membrane fuel cells
 HT-PEMFC: high temperature proton exchange membrane fuel cell
 PA: phosphoric acid
 PA/PBI: phosphoric acid-doped polybenzimidazole
 PA/CBrPBI-X: phosphoric acid-doped macromolecular cross-linked PBI membranes
 NGDE: 1,3-bis(2,3-epoxypropoxy)-2,2-dimethylpropane
 TMBP: 4,4'-diglycidyl(3,3',5,5'-tetramethylbiphenyl) epoxy resin
 DAB: 3,3'-diaminobenzidine
 DPIP: diphenyl-m-phthalate
 TMbP: 3,3',5,5'-tetramethyl-4,4'-biphenol
 NBS: N-bromosuccinimide
 DFBP: 4,4'-Difluorobenzophenone
 BPO: benzoyl peroxide
 K_2CO_3 : anhydrous potassium carbonate
 DMAc: N,N-dimethylacetamide
 $CDCl_3$: deuteriochloroform
 TMS: tetramethylsilane
 $DMSO-d_6$: deuterated dimethyl sulfoxide
 FT-IR: Fourier transform infrared
 TGA: thermogravimetric analysis